HIGH PRESSURE LIQUID CHROMATOGRAPHIC STUDIES OF COAL LIQUEFACTION KINETICS

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Introduction

A major obstacle to the advancement of coal conversion technology has been the lack of effective means for analyzing the highly complex mixtures occurring in coal conversion processes. High pressure liquid chromatography (HPLC) is a recently developed analytical tool that typically provides rapid, reproducible analysis of complex systems (1,2). Using HPLC, preparatory experiments can be performed to separate 50-100 mg samples of relatively pure compounds from a complex mixture - allowing subsequent positive identification of the compounds by other means such as infrared or ultraviolet spectroscopy, and melting point. This asset of HPLC (ie., preparatory scale chromatography) is one of the main advantages that it offers over comparable analytical methods. Because HPLC does offer positive identification of individual species, it is a very effective tool for characterizing and quantifying process streams in coal liquefaction processes, and provides a means for developing a more fundamental understanding of such processes.

The present work demonstrates the feasibility of employing HPLC to characterize creosote oil, a coal-derived liquid used as a start up solvent in coal liquefaction processes such as the Solvent Refined Coal (SRC) process. Characterization of the creosote oil is done by HPLC during hydrogenation/hydrodesulfurization of the oil; and is then used to follow the catalytic effects of a commercial Co-Mo-Al catalyst; a coal mineral, iron pyrite; coal ash; and actual SRC mineral residue from the Wilsonville pilot plant. Each of these agents has a significant effect on the hydrogenation and, except for pyrite, on the hydrodesulfurization of creosote oil under conditions similar to those in the SRC process. Evidence that coal minerals have a catalytic effect on hydrogenation of coal has been reported (3,4). However, specifically which compounds in recycle or process solvent are most

affected by hydrogenation in the presence of coal minerals has not been previously studied. Also the effect of coal mineral catalysis on rate of removal of various heteroatom compounds - particularly sulfur bearing compounds such as dibenzothiophene - has not been studied. HPLC provides a tool for monitoring changes in major constituents of coal-derived liquids during hydrogenation/hydrodesulfurization, and can be used to study the selectivity of catalytic agents for accelerating reactions involving specific species of coal-derived liquids - as is demonstrated here.

Experimental

Apparatus. A Model ALC/GPC-201 high speed liquid chromatograph (Waters Associates, Milford, Mass.) was used throughout this study. The following accessory hardware was used: a Model 6000 solvent delivery system, a Model 660 solvent programmer, and a Model U6K injection system. In addition, a Model GM77 UV/VIS detector (Schoeffel Instrument Corporation, Westwood, N.J.) was used; this detector was chosen because it has a continuously variable UV source. After thorough exploratory studies, a wavelength setting for the detector of 232 nm was found to provide the best overall sensitivity and stability for detection; this setting was used throughout the study.

Reagents. The acetonitrile used in this study was of spectroquality. The creosote oil was obtained from Southern Services, Inc., at the SRC pilot plant located at Wilsonville, Alabama. Southern Services, Inc., obtained the oil, creosote oil 24-CB, from the Allied Chemical Company. The oil has a boiling point range of 175° to 400°C and a specific gravity of 1.096 at 20°C. Hydrogen was obtained from Linde Hydrogen in 6000 psi grade, with a purity of 99.995%.

A commercial Co-Mo-Al catalyst (Comox-451) was obtained from W. R. Grace and Company, Davidson Chemical Division, Baltimore, Maryland. This catalyst is commercially produced by Laporte Industries of England. Our analysis of the catalyst showed that it consists of 3.7% CoO and 12.8% MoO_3, and the catalyst was specified by the manufacturer to have a surface area of 300 m^2/g and a total pore volume of 0.66 ml/g. The pyrite used in these experiments was obtained from Matheson Coleman and Bell Chemical Company, Norwood, Ohio. Our analysis of the pyrite showed that it was 90-95% pure, the difference being primarily silica. Coal ash was obtained by burning a mixture of Kentucky No. 9/14 coal mixture (7.2% ash) in a muffle furnace at 1000°C. Analysis of the ash gave an iron content of 13.7%. SRC solids were obtained from the filter cake from the Wilsonville, Alabama SRC Pilot Plant. Analysis of the material gave an ash content of 55.2% and a sulfur content of 13.6% The reported analysis of this material showed that it was 30% filter aid (diatomaceous earth) (5). All materials were ground and screened; and only -325 mesh (45 micron) size material was used.

High Pressure Liquid Chromatography. Two 4mm (ID) X 30 cm microbondapak/C_{18} columns (Waters Associates, Milford, Mass.) were used in series for separation of the creosote oil components. The mobile-phase was a 45:55 volume-to-volume acetonitrile-water mixture. The

flow rate was nonlinearly (curve 8 on the 660 solvent programmer) programmed to increase from 0.6 to 0.8 ml/min in 1.5 hours in such a way that the major portion of the increase takes place in the last 45 minutes of the program. This allows for the most efficient use of the time necessary for elution by minimizing dead-time and axial diffusion - while keeping resolution at a miximum during the initial portion of the separation. System pressure was kept below a maximum of 2200 psi.

The sample was dissolved in pure acetonitrile (4mg/ml) prior to injection, and normally about 10 μl of the resulting solution was injected for analysis. Retention times ranged from as short as a few minutes for the more polar compounds to as much as several hours for the more nonpolar compounds, which are typically the higher molecular weight constituents.

Procedure. Creosote oil was treated for two hours at 425°C under an initial pressure of 3000 psig of hydrogen, in the presence of 13% by weight of either Co-Mo-Al catalyst, iron pyrite, coal ash, or SRC solids. Treatment was also made without any catalytic agents present. The reaction mixtures were stirred continuously at 2000 rpm in a batch autoclave (Autoclave Engineers, Erie, PA.). After two hours of reaction, samples of the partially hydrogenated and hydrodesulfurized oil were taken. Then, aliquot amounts of these samples were dissolved in acetonitrile (4mg/ml), filtered through 0.5μ filters (Millipore Intertech, Inc., Bradford, MA.) to remove any solids; and after filtration, 10μl portions of the filtrate were analyzed by HPLC. To eliminate unaviodable variations due to differences in the amount of sample injected, benzofuran was used as an internal standard.

Computer Deconvolution. As is seen in Figure 1 the chromatograms obtained in this work gave peaks that seldom had base-line resolution - a common problem in chromatography - and, to be accurate, it was necessary to deconvolute the chromatograms. To this end, a specialized computer program was developed (6) based on the method of Marquardt (7).

Results and Discussion.

Typical chromatograms of the product from the various treatments of the creosote oil are shown in Figure 1. Good separation of the multicomponent system was obtained by varying the acetonitrile/water ratio in the eluting solvent: the best resolution resulted with a 45:55 volume-to-volume acetonitrile-water mixture. Preparatory scale columns were used to obtain sufficient amounts of twelve major constituents to permit their positive identification by infrared spectroscopy. These major constituents, which compose 50.3% by weight of the original creosote oil, were of interest in this preliminary work (Table 1).

The components fall into basically two categories: polynuclear aromatics and heteroatom compounds. Compounds of the first type -

namely, naphthalene, acenaphthene, phenanthrene, and anthracene -
are angular polycyclic aromatics. These compounds, and compounds
like them, are considered to play an important role in hydrogen trans-
fer reactions occurring during coal liquefaction, e.g. as in the SRC
process (8,9,10). Compounds of the second type - namely, dibenzothio-
phene, carbazole and naphthonitrile - are of interest because these
constituents, during combustion of coal, form pollutants, SO_2 and
NO_x. Determination of the degree to which these constituents are
removed with processing is therefore most important for process an-
alysis.

The results from this work and those from previous analysis
using gas chromatography are compared in Table 2. In evaluating this
comparison, it should be noted that the creosote oil is somewhat un-
stable: after standing for long periods of time (several months) some
constituents do indeed precipitate from solution. For this reason
some discrepancies exist between our gas chromatographic analysis,
that performed by Allied Chemical Company, and that performed by
Southern Services.

Table 1 lists the analysis of the creosote oil after the various
treatments. Obviously, hydrogenation and hydrodesulfurization of the
creosote oil at 425°C in the presence of an initial hydrogen partial
pressure of 3000 psig causes a significant decrease (20%) in percent
by weight of the analyzed components. Currently, preparatory scale
work is in progress to determine what compounds are produced by this
treatment. In the presence of the various catalytic agents, even more
reduction (34%, when pyrite is present, to 49%, when actual SRC min-
eral residue is present, as compared to 20%, when no catalyst is
present) in the weight percent of the analyzed components results
during hydrogenation of the oil. Apparently then, these agents (Co-
Mo-Al, pyrite, coal ash, and SRC mineral residue) do indeed catalyze
hydrogenation of the oil, and the increase in hydrogen consumption
observed when they are present is, in fact, due to greater hydrogen-
ation of the oil, rather than reduction of the agent, itself, with
hydrogen to produce a reduced form of the agent, water, hydrogen
sulfide, etc.

As shown in Table 1, HPLC offers sufficient specificity to detect
differences in the final concentration of major constituents of the
oil when hydrogenated in the presence of the different catalytic
agents. For example: Assuming that the disappearance of the major
constituents is due to hydrogenation, then Co-Mo-Al, coal ash, and
SRC mineral residue show a decisive preference for accelerating
hydrogenation of naphthalene, 1-methylnaphthalene, and 2-methylnaph-
thalene; whereas pyrite favors hydrogenation of acenaphthene and,
to a lesser extent, anthracene. Also, in the presence of commercial
Co-Mo-Al catalyst, the concentration of dibenzothiophene, a major
organic sulfur component, is reduced to a much greater extent than
when the other catalysts were present. In fact, the concentration
of dibenzothiophene was reduced essentially to zero when Co-Mo-Al
was present. Since Co-Mo-Al is an excellent catalyst for hydrode-
sulfurization reactions, these results are not surprising. Most
interestingly, however, the trend in dibenzothiophene removal is

exactly the same as that found by analysis of total sulfur (4): namely, Co-Mo-Al >> coal ash > SRC mineral residue > pyrite > H_2 only. Carbazole, on the other hand, has essentially the same concentration as that in the original oil, despite the catalyst used; whereas the naphthonitriles are completely removed when either Co-Mo-Al, coal ash, or SRC mineral residue is present.

Conslusions

The HPLC procedure described here permits analysis of major constituents of creosote oil in about two hours. No extensive sample preparation is required; and the method is quantitative - the results comparing well with those obtained using gas chromatography. Using preparatory chromatography, samples of essentially pure compounds can be separated from creosote oil and positively identified by subsequent analysis. As a result, with HPLC neither tentative identification as, for example, by "spiking" - i.e. addition of known compounds to the mixture so as to determine the peaks in the chromatogram of the mixture caused by different constituents - nor an expensive, sophisticated gas-chromatograph/mass-spectrometer system are required. Hence HPLC offers a simple and powerful technique for analysis of complex mixtures like creosote oil.

Acknowledgments

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TABLE 1

HPLC Analysis of Treated Creosote Oil

Compound	Wt. %					
	A	B	C	D	E	F
1 and 2-naphthanitrile	0.611	0.458	0.243	trace	0.046	trace
carbazole	0.423	0.386	0.418	0.386	0.443	0.526
naphthalene	8.92	7.49	6.55	4.16	4.01	4.17
2-methylcarbazole	0.106	0.084	0.059	0.067	0.102	trace
1-methylnaphthalene	5.23	4.56	3.14	3.13	2.33	2.08
2-methylnapthalene	8.00	6.21	7.63	5.42	4.61	4.37
acenaphthene	6.28	4.15	1.56	2.38	2.24	2.08
fluorene	5.22	5.02	3.78	3.62	3.64	4.55
dibenzothiophene	1.27	0.888	0.720	trace	0.576	0.622
phenanthrene	12.4	9.10	7.95	8.05	7.11	5.96
anthracene	1.86	1.88	1.31	2.17	1.50	1.53
Total	50.32	40.23	33.36	29.39	26.61	25.89

A – original oil
B – oil heated with hydrogen, no catalyst
C – oil heated with hydrogen and pyrite
D – oil heated with hydrogen and cobalt molybdate
E – oil heated with hydrogen and coal ash
F – oil heated with hydrogen and SRC solids

Three runs were made for each treatment with a relative standard deviation between runs of $\pm$ 8% of the determined mean weight per cent.

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TABLE 2

Comparison of Creosote Oil Analyses

Compound	Wt. %			
	A	B	C	D
1 and 2-naphthonitrile	0.32	-	0.61	-
carbazole	2.2	-	0.42	-
naphthalene	5.1	9.08	8.92	10.0
2-methylcarbazole	1.7	-	0.11	-
1-methylnaphthalene	0.38	3.55	5.23	3.0
2-methylnaphthalene	1.3	10.2	8.00	8.0
acenaphthene	6.0	9.73	6.28	5.0
fluorene	10.3	5.54	5.22	5.0
dibenzothiophene	0.52	0.94	1.01	-
phenanthrene	18.6	17.92[a]	12.45	17.0[a]
anthracene	4.3		1.86	

A - Allied Chemical Company by gas chromatography
B - Southern Services by gas chromatography (ASTM D2887)
C - Auburn University by HPLC
D - Auburn University by gas chromatography
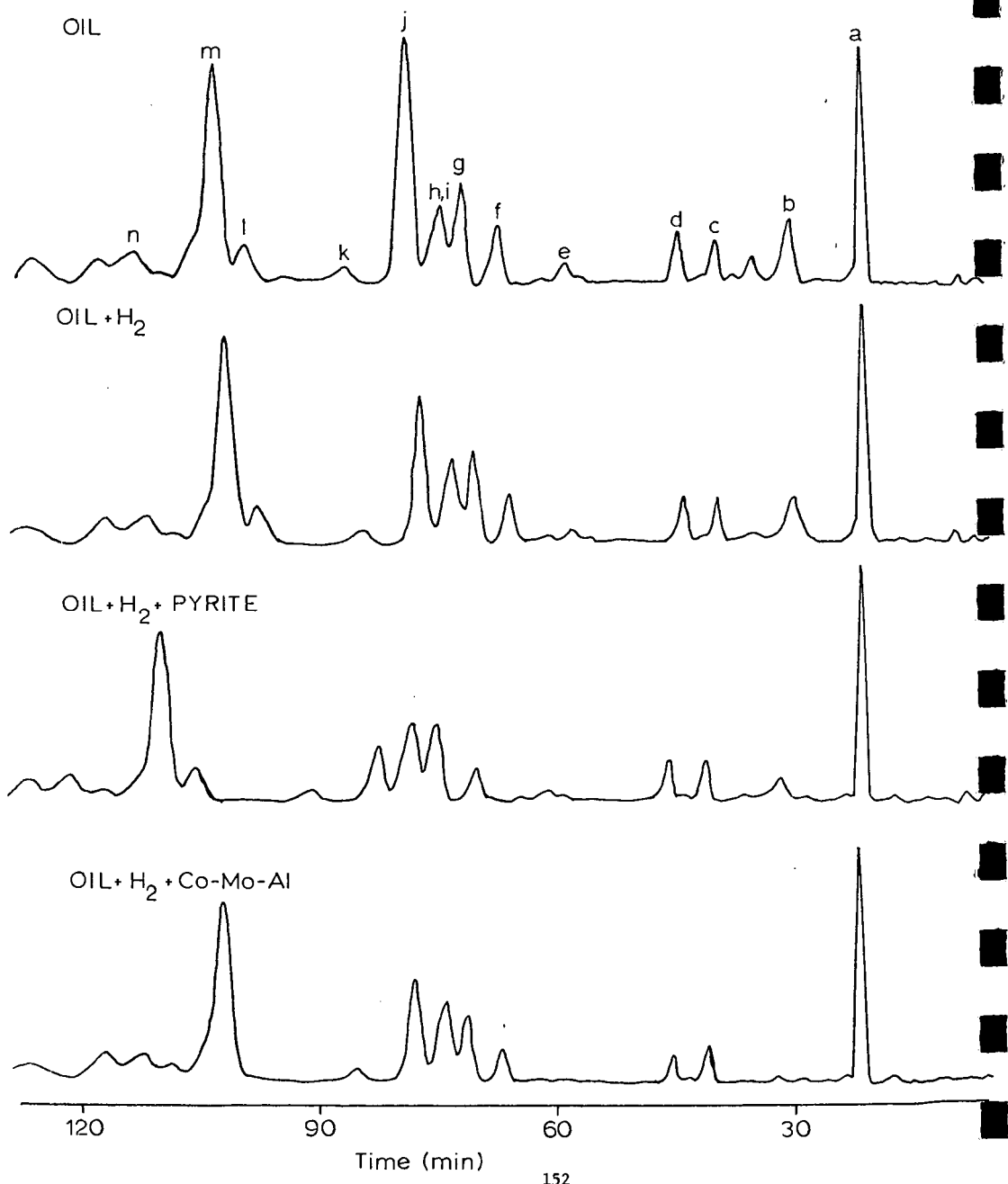
a - includes both phenanthrene and anthracene

OIL

OIL + H$_2$

OIL + H$_2$ + PYRITE

OIL + H$_2$ + Co-Mo-Al

Time (min)

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Figure 1

Chromatograms of creosote oil which show the effect of the various treatments. Positively identified components in order of elution are:

a. internal standard (benzofuran)
b. 1 and 2-naphthonitrile
c. carbazole
d. naphthalene
e. 2-methylcarbazole
f. 1-methylnaphthalene
g. 2-methylnaphthalene
h. dibenzofuran
i. biphenyl
j. acenaphthene
k. fluorene
l. dibenzothiophene
m. phenanthrene
n. anthracene